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Chemical Modification of Lignin-Rich Paper
Part 10: The Light-Induced Yellowing of Untreated and Acetylated High-Yield Pulps
Studied by Solid-State UV/VIS Diffuse Reflectance Spectroscopy

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Chemical modification of lignin-rich paper

Part 10. The light-induced yellowing of untreated and acetylated high-yield pulps studied by solid-state UV/VIS diffuse reflectance spectroscopy

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SUMMARY: Untreated and acetylated hydrogen-peroxide-bleached aspen CTMP and hydrogen-peroxide-bleached spruce CTMP were subjected to accelerated light-induced aging using three different types of light-sources (UV-fluorescent lamps, $\lambda_{\text{max}}=350$ nm and UV/VIS-fluorescent lamps $\lambda_{\text{max}}=425$ and 575 nm). The photochemical changes that took place during acetylation and irradiation were followed by solid-state UV/VIS diffuse reflectance spectroscopy.

The wavelength distribution of the irradiation source strongly influenced the photochemistry of both untreated and acetylated pulps. Absorption difference spectra of aspen CTMP, irradiated with the UV-lamps, exhibited an apparent absorption maximum at 370 nm with a shoulder at 415 nm, whereas the UV/VIS-fluorescent lamps irradiated aspen CTMP exhibited an absorption peak at 360 nm and substantially less absorption in the entire visible region ($\lambda > 400$ nm). Two major absorption peaks, at 330-345 nm and at 425 nm, were observed in the UV/VIS absorption difference spectra of irradiated spruce CTMP regardless of the irradiation source used. However, in addition to the photodiscoloration, a photobleaching with $\lambda_{\text{max}} \sim 390$ nm was observed when the spruce CTMP was irradiated with the two types of UV/VIS-fluorescent lamps. Acetylation was found to slow down the UV-light induced reactions, but could also promote photobleaching reactions when subjected to an irradiation source emitting light in the visible range. Generally, no further discoloration was observed when the acetylated CTMPs (acetyl content, 8-10%) were irradiated with the UV/VIS-fluorescent lamps under the aging conditions used in this work.

This investigation has shown the importance of choosing a light source that resembles the actual reversion situation as close as possible (e.g., contain both an ultraviolet and a visible component) if realistic accelerated light-induced reversion conditions are to be obtained.

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During the last decade, pulping processes have been developed that can produce high-performance, lignin-containing pulps (e.g., hydrogen-peroxide-bleached chemithermomechanical pulps, CTMP) at significantly lower capital and operating costs than kraft pulps. Mechanical pulps use the forest resources more efficiently, and because of the use of nonchlorine-based bleaching chemicals, full mill closure is currently possible (Stevenson 1992). Further, the simple process technology allows for economical construction of new pulping capacity in small units (ca. 250 tons/day). Hardwood high-yield pulps can be bleached to a brightness level of 86-88% ISO, i.e., sufficiently high for most high-quality communication papers. Furthermore, at a substitution degree of 25% in the sheet, high-yield hardwood pulps can offer the papermaker a substantial economical savings in the range of \$10-40/ton of paper (Ford, Sharman 1996).

In spite of the many positive features these new generation of high-yield pulps possess, mechanical pulps are mainly used for the production of short-lived, low-value paper grades. This is because a lengthy exposure to daylight (i.e., ultraviolet light) causes a discoloration (yellowing) that is unacceptable in many applications. It is mainly light-induced reactions in the lignin part of the pulp constituents that causes the discoloration (cf. Heitner, Schmidt 1991; Leary 1994).

There still are uncertainties about the reactions leading to colored structures during photoyellowing or what the final chemical structures of the colored products are. It was early suggested that quinones, quinone methides, and cyclohexadienones generated from phenoxyl radicals are the initially formed colored products (Leary 1968a; Leary 1968b; Lin, Kringstad 1971). Irradiation of lignin model compounds in the presence of oxygen showed that different types of reactions could occur in the photooxidation process (Lin, Kringstad 1971). First, a demethylation reaction that generates *ortho*-quinonoid structures. This is in accordance with the loss of methoxyl groups observed for irradiated groundwood (Forman 1940; Lewis, Fronmuller 1945; Leary 1968a). It is also possible that *para*-quinonoid structures, formed through side-chain displacement, could contribute to color formation although to a lesser extent than *ortho*-quinonoid structures (Lin, Kringstad 1971). Other investigations have, however, stated that side-chain elimination to produce primarily hydroquinones (*para*-quinones) is the main reaction pathway during photoyellowing (Gellerstedt, Pettersson 1977, cf. Forsskåhl et al. 1991; Hirashima, Sumimoto 1994; Agarwal 1997). A third possibility is 5-5 coupling of phenoxyl radicals to form colored biphenyl compounds (cf. Forsskåhl 1994).

Exposure of CTMP and TMP (thermomechanical pulp) to ultraviolet radiation with a wavelength of 300-400 nm produced chromophores with absorption maxima at 350 and 420 nm (Heitner, Min 1987). These chromophores were considered to be a methoxy-*p*-benzoquinone and an *ortho*-quinone with an aliphatic substituent in the 2-position. *Ortho*-quinonoid structures have been detected in different types of high-yield pulps, both before and after irradiation. Lebo et al. (1990) found that about 75% of the increase in color during irradiation of white spruce refiner mechanical pulp was caused by the formation of *ortho*-quinones. Zhu et al. (1995) used fluorescence spectroscopy to confirm the presence of photochemically generated *ortho*-quinones in several hydrogen-peroxide-bleached high-yield pulps. Schmidt et al. (1995) reported that both methoxylated and unmethoxylated *ortho*-quinones were likely to be introduced in peroxide-bleached mechanical pulps during irradiation. Monomeric *ortho*-quinones were suggested to be the major chromophores formed during light-induced yellowing of lignin-rich pulps based on UV/VIS reflectance spectroscopy of peroxide-bleached GWP (groundwood pulp), CTMP, and quinonoid lignin model compounds (Zhang, Gellerstedt 1994a). Stilbene *ortho*-quinones were reported to be the only colored products formed when monohydroxystilbenes (deposited on the surface of a filter paper) were exposed to UV radiation (Zhang, Gellerstedt 1994b). Furthermore, the

chromophores produced by UV radiation were found to be almost completely removed by sodium borohydride reduction (Hemmingson, Morgan 1990; Capretti et al. 1994; Schmidt, Heitner 1995; Pan, Ragauskas 1997). This suggests that most of the colored substances formed contain carbonyl structures (quinones, conjugated ketones, aldehydes) that can be reduced by NaBH₄.

Argyropoulos et al. (1995) used solid-state ³¹P NMR spectroscopy on samples of irradiated unbleached and hydrogen-peroxide-bleached GWP (oxyphosphorylated) in order to determine the early photochemical changes that occur during light-induced yellowing. The data suggested that *ortho*-quinones initially produced during irradiation subsequently reacted to form more complex carbonyl chromophoric structures which do not have a quinonoid character. It was also found that *ortho*-quinones were converted faster in the unbleached pulp than in the peroxide-bleached pulp. The bleached pulp contains more stilbenes that could be converted to stilbene *ortho*-quinones during irradiation (Zhang, Gellerstedt 1994b), and it is possible that these structures require longer irradiation times to be eliminated. The conversion of quinones to more complex chromophores could explain why no quinones or quinonoid structures were detected in irradiated milled wood lignin (Sjöholm et al. 1992).

Forsskåhl and Janson (1991a) reported that the two main chromophores (displaying bands at 370 and 430 nm), generated by irradiation of chemimechanical pulps, were interrelated. Irradiation at a short wavelength (373 nm) creates a colored chromophore, while irradiation at the longer wavelength (435 nm) leads to the formation of a colorless product. These authors suggest that there are several possible candidates for such a system; a hydroquinone-quinone system, charge transfer complexes, possibly quinone methides and also cis-trans isomerism of aromatic conjugated double bonds. The same effect was later found for irradiated unbleached and peroxide-bleached thermomechanical pulps (Forsskåhl, Maunier 1993). Schmidt et al. (1995) reported that methoxylated *ortho*-quinones could be bleached by 420 nm irradiation, whereas unmethoxylated *ortho*-quinones sensitized destruction of aromatic groups. Robert and Daneault (1995) observed two major absorption peaks at 360 and 425 nm when TMP paper (black spruce/balsam fire mixture) was exposed to UV light (λ , 300-400 nm). The peak at 360 nm was the result of the disappearance of one chromophore and the appearance of a different chromophore. The other peak (425 nm) was the result of the formation of three chromophores.

It is important to bear in mind that quinonoidic structures are themselves photosensitizers and that they can thus contribute to further chromophore formation (Gierer, Lin 1972; Neumann, Machado 1989; Ek 1992; Forsskåhl et al. 1993; Castellan et al. 1993).

The present communication describes the effect of acetylation on the light-induced yellowing of hydrogen-peroxide-bleached aspen CTMP and hydrogen-peroxide-bleached spruce CTMP, the pulps most often suggested as replacement for chemical pulps in high-quality paper grades. The mechanism of stabilization (and yellowing) has been studied using solid-state UV/VIS diffuse reflectance spectroscopy performed on high basis weight (200 g·m⁻²) handsheets. The effect of three irradiation sources with different wavelength distributions on the light-induced yellowing will also be discussed.

Experimental

Pulps and paper samples. Commercially produced hydrogen-peroxide-bleached spruce (*Picea abies*) and aspen (*Populus tremuloides*) CTMP were used as received for the studies described in this paper. The pulps were obtained as dried samples. The high-brightness hardwood CTMP was manufactured employing hydrogen peroxide both as a chemical pretreatment and as a bleaching stage. Handsheets (200 g·m⁻²) were prepared according to

TAPPI Test Method T 205 om-88. The paper sheets were then conditioned at 23°C and 50% r.h. according to TAPPI Test Method T 402 om-88 before further treatment.

Acetylation procedure. The handsheets [cut into strips (30 x 75 mm)] were acetylated (at 100°C) according to the procedure described by Paulsson et al. (1994).

Analyses. The acetyl content was calculated from the amount of acetate liberated after saponification with sodium hydroxide as previously described in Paulsson et al. (1996a). The acetyl content is given as a percentage of the dry weight of the paper.

UV/VIS diffuse reflectance spectroscopy. UV/VIS spectra were recorded on a Perkin Elmer Lambda 19 DM spectrophotometer equipped with a diffuse reflectance and transmittance accessory (Labsphere RSA-PE-90). The accessory is essentially an optical bench which includes double beam transfer optics and a six-inch diameter (154 mm) integrating sphere. Background correction was made with a SRS-99-010-7890 standard. The absorbance (*ABS*) was calculated from the diffuse reflectance (R_∞) using the following expression derived from the Beer-Lambert law (cf. Robert, Daneault 1995): $ABS = -\log R_\infty$. The resulting spectra were averaged from four to six measurements.

Accelerated light-induced yellowing. The paper samples were subjected to an accelerated photoyellowing in a Rayonet photochemical reactor (Model RPR 100, The Southern New England Ultraviolet Company, Branford, CT, USA) equipped with eight RPR 3500Å UV-fluorescent (“blacklight”) lamps, eight RPR 4190Å UV/VIS-fluorescent lamps, or eight RPR 5750Å UV/VIS-fluorescent lamps and a merry-go-round apparatus for uniform irradiation. All lamps were obtained from The Southern New England Ultraviolet Company. The temperature was kept close to room temperature by a cooling fan (to minimize heating of the sample). The temperatures were 29°C, 31°C, and 27°C for the RPR 3500Å, RPR 4190Å, and RPR 5750Å lamps aged sheets, respectively. *Fig. 1* summarizes the spectral distribution of the three light sources, as received from the manufacturer. The spectral distribution of standard “cool white” fluorescent color used in many commercial lighting installations (Waymouth 1992, dotted line in *Fig. 1*) and natural daylight (Merrigan 1975, broken line) is given as a comparison. Untreated paper sheets were used in all radiation experiments as controls.

Optical measurements. TAPPI brightness and color changes according to the CIELAB color scale (L^* -, a^* -, b^* -values) were measured using a Technidyne Brightimeter (Model S-5) according to TAPPI Test Method T 452 om-92 and TAPPI Test Method T 524 om-94, respectively.

Results and discussion

Fig. 1 shows the relative energy distribution of the three irradiation sources used for accelerated aging in this work. The RPR 3500Å UV-lamps emit light in a band between 300 and 420 nm with an approximately Gaussian spectral distribution ($\lambda_{\max}=350$ nm). The lamps lack, however, the visible component of diffuse sunlight or office light. The RPR 4190Å UV/VIS-lamps have a slightly narrower emission band with a maximum at approximately 425 nm. The third irradiation source, RPR 5750Å, emits light in both the ultraviolet and visible range (from about 350 to 700 nm, $\lambda_{\max}=575$ nm) and has a comparatively close match to the conventional standard “cool white” fluorescent color used in many commercial lighting installations (see dotted line in *Fig. 1*).

Absorption difference spectra of untreated, irradiated pulps

The interpretation of a UV/VIS absorption spectra at short wavelengths (e.g., below 340 nm) is difficult since the signal to noise ratio is low in this region (Robert, Daneault 1995). This is because the paper sample absorbs most of the light due to its thickness and its high lignin concentration. A complement to this study, in the low wavelength range, could be performed using low basis weight sheets ($10 \text{ g}\cdot\text{m}^{-2}$) according to the procedure described by Schmidt and Heitner (1993a). Care should also be taken when evaluating the results after high UV exposures since the assumption of exponential distribution of chromophores in the thickness of the sheet may no longer be valid (cf. Robert, Daneault 1995). Nevertheless, solid-state UV/VIS diffuse reflectance spectroscopy, performed on thick handsheets and with the consideration of the above limitations, is a powerful technique for the study of light-induced yellowing of lignin-containing materials. The result that is obtained with this method is what the eye will perceive as “yellowing of a thick paper.”

Figs. 2a-c show the UV/VIS absorption difference spectra (ΔABS vs. wavelength) of hydrogen-peroxide-bleached aspen CTMP recorded after aging with various light sources. The change in optical properties on acetylation and irradiation is given in *Table 1*. It is evident that the choice of irradiation source strongly influenced the photochemistry. Although all of the light sources generated a discoloration in the entire visible region ($\lambda > 400 \text{ nm}$), the shape of the absorption curves was different. Irradiation with the RPR 3500Å UV-lamps generated an apparent absorption maximum at 370 nm with a shoulder at approximately 415 nm (*Fig. 2a*), whereas the RPR 4190Å and RPR 5759Å UV/VIS-lamps generated an absorption maximum at 360 nm and showed substantially less absorption in the $\lambda > 400 \text{ nm}$ range (*Figs. 2b-c*). The spruce CTMP behaved somewhat differently as can be seen in *Figs. 3a-c*. Irradiation with the RPR 3500Å UV-lamps generated an apparent maximum at 330 nm and a distinct maximum at 425 nm. The RPR 4190Å and RPR 5759Å UV/VIS-lamps introduced two maxima; one at 330 nm that was shifted toward longer wavelengths (345 nm) after extensive reversion, and one at 425 nm. In addition to the photodiscoloration, a photobleaching with $\lambda_{\text{max}} \sim 390 \text{ nm}$ was observed for the last two light sources (*Figs. 3b-c*).

Several research groups have used UV/VIS diffuse reflectance spectroscopy to study the yellowing phenomena. Schmidt and Heitner (1995) reported that hydrogen-peroxide-bleached aspen CTMP showed a single maximum at about 360 nm when exposed to broadband UV radiation, but no shoulder at $\sim 415 \text{ nm}$ was detected. The high-brightness aspen CTMP used in the present investigation was pretreated with hydrogen peroxide, and it is possible that this treatment changes the chromophoric precursors in such a way that new colored substances, absorbing in the 415 nm region, were formed when subjected to UV-exposure. Generally, UV/VIS diffuse reflectance spectroscopy of hydrogen-peroxide-bleached softwood pulps (GWP, TMP, and CTMP) performed on both thin and thick sheets, shows an increased absorption in the UV region at 320-360 nm and in the visible region at 410-435 nm when exposed to UV-radiation (Hirashima, Sumimoto 1986; Heitner, Min 1987; Fournier de Violet et al. 1989; Forsskåhl, Janson 1991b; Francis et al. 1991; Schmidt, Heitner 1991; Schmidt, Heitner 1993a,b; Zhang, Gellerstedt 1994a; Robert, Daneault 1995; Schmidt, Heitner 1995; Schmidt, Heitner 1997). The increase in absorption in the UV-region has been attributed to the formation of aromatic carbonyl groups ($\lambda_{\text{max}} \sim 330 \text{ nm}$) and to the formation of quinones [possibly methoxylated *para*- or *ortho*-quinones (monohydrate adduct see Schmidt, Heitner 1995, cf. Adler, Lundquist 1961), $\lambda_{\text{max}} \sim 350\text{-}370 \text{ nm}$]. It is also possible that coniferaldehyde with an absorption maximum at $\sim 350 \text{ nm}$, generated through photooxidation of coniferyl alcohol, contributes to the UV-absorption peak. The increase in the absorption in

the visible region is attributed to the formation of *ortho*-quinonoidic chromophores, at least in an initial phase.

The present investigation showed that regardless of the wavelength distribution of the irradiation source, absorption peaks appeared in the above-mentioned UV and visible regions during aging of hydrogen-peroxide-bleached spruce CTMP. The relationship between the peak areas and the position of the maxima was, however, dependent on the light source used. The photobleaching observed at short irradiation times for the two UV/VIS-lamps was somewhat more pronounced for the RPR 4190Å lamps. This was expected since these lamps emit light in the region where photobleaching is noticeable (Andrady et al. 1991; Forsskåhl, Janson 1991a). The decrease in absorption at 360 nm observed during irradiation of lignin-containing materials has been attributed to the destruction of coniferaldehyde end groups or to the conversion of quinones to colorless structures (Wang et al. 1995, cf. Castellan et al. 1993; Ragauskas 1993). The reduction in chromophore content at 390 nm cannot entirely be explained by the elimination of these structures since sulfonation and hydrogen peroxide bleaching eliminate most of the coniferaldehyde and quinonoidic structures (cf. Dence 1996). Hydroxystilbenes, that can be introduced in the lignin moiety during high-yield pulping and alkaline bleaching conditions (Gellerstedt, Agnemo 1980; Wu et al. 1991; Gellerstedt, Zhang 1992), have been proposed as the leucochromophore that, to a large extent, are responsible for the initial discoloration of bleached high-yield pulps (Gellerstedt, Zhang 1993, cf. Castellan et al. 1990). Simple stilbenes have an absorption maximum at about 330 nm in solution, but it is possible that this maximum can be shifted to higher wavelengths when incorporated in the lignin macromolecule due to steric and electronic effects of substituent groups. Zhang and Gellerstedt (1994a) reported a red-shift of the UV/VIS absorption maxima of quinone and stilbene model compounds in the solid state (on filter paper or on bleached GWP or CTMP) compared with the absorption in solution. The red-shift was 26 nm for a hydroxystilbene model and between 32 and 148 nm for quinonoidic compounds, an effect charge transfer complexes (quinone-phenol) might account for (Zhang, Gellerstedt 1994a; cf. Furman, Lonsky 1986; Furman, Lonsky 1988).

It is evident that measurements of brightness and L^* -, a^* -, and b^* -values hardly can give a complete and accurate description of a complicated photochemical process such as the discoloration of lignin-containing materials. For example, the brightness level of the irradiated spruce CTMP handsheets was approximately the same (46.7-48.5%, see *Table 1*) for the three light sources when compared at different reversion times. However, the photochemistry was not the same as can be seen in *Fig. 4*. Furthermore, it is also questionable to use a light source that only emits light in the ultraviolet range for reversion studies since the photochemistry in the presence of visible light is quite different and it may lead to the wrong conclusion regarding the reaction mechanism(s) and degree of yellowing (stabilization) (cf. Paulsson, Ragauskas 1998a). However, the UV-lamps give an assessment of the UV light-aging properties and could be useful when complications from other wavelengths are not desirable.

Absorption difference spectra of acetylated pulps

It is known that the acetylation process influences brightness differently depending on the type of mechanical pulp derivatized (unbleached-bleached, softwood-hardwood, see Manchester et al. 1960; Paulsson et al. 1996a; Paulsson, Ragauskas 1998a). *Fig. 5* shows the UV/VIS absorption spectra (difference acetylated - unacetylated) for the two tested pulps. During acetylation of aspen CTMP, a substantial increase in the absorption is seen in the entire wavelength range 350-700 nm with maxima at approximately 370 and 430 nm. This corresponds to a decrease in brightness with 8 and 11 brightness units for a reaction time of 5

and 20 minutes, respectively (*Table 1*). The large loss in brightness for the hydrogen-peroxide-pretreated aspen pulp is contradictory to earlier reported results for hydrogen-peroxide-bleached high-yield pulps (cf. discussion in Paulsson, Ragauskas 1998b). Acetylation of the spruce CTMP induced a discoloration, indicated by the absorption increase at $\lambda > 410$ nm, but also a bleaching at wavelengths below 410 nm (maximum at approximately 385 nm). Acetylation of model compounds, representative of chromophoric and leucochromophoric structures in lignin, has shown that catechols, hydroquinones, stilbenes, and coniferyl alcohol units were rapidly derivatized on acetylation (Paulsson et al. 1996b). Models of the *ortho*-quinonoid type, both methoxylated and unmethoxylated, were also rapidly decomposed and, to a large extent, decolored on acetylation, whereas structures of the *para*-quinonoid type were essentially unaffected. Further, a coniferaldehyde model was slowly derivatized yielding a derivative of the acylal type. Based on the above findings, the decrease at 385 nm could possibly be explained by the removal of a hydroxystilbene structure (cf. the discussion above dealing with a red-shift of the absorption maxima of stilbenes in the solid state). The peaks at 370 and 430 nm could result from the characteristic UV absorption of methoxylated *para*-quinones and visible absorption of *ortho*-quinones, respectively. The absorption peak at 455 nm is close to the absorption peak of a stilbene *ortho*-quinone structure incorporated on bleached CTMP ($\lambda_{\text{max}} = 460$ nm, see Zhang, Gellerstedt 1994a).

Absorption difference spectra of acetylated, irradiated pulps

Figs. 6a-c and *7a-c* show the effect of different irradiation times and different irradiation sources on the UV/VIS absorption difference spectra of acetylated aspen CTMP and acetylated spruce CTMP, respectively. The photoaging properties for the low acetylated sheets (5 minutes) were, in general, the same, although shifted to a somewhat lower stability level as indicated by the lower acetyl content and will therefore not be discussed further. However, UV/VIS spectra for the low acetylated test sheets irradiated for the longest time (24, 349, and 312 hours depending on light source) are given as a comparison in *Figs. 6* and *7*.

It was interesting to see if acetylation, an efficient way to retard yellowing of different types of high-yield pulps, fundamentally changed the photochemistry or only slowed down the rate of chromophore formation, as judged from the UV/VIS absorption spectra. The acetylated aspen CTMP, irradiated with the RPR 3500Å UV-lamps, generated an apparent absorption maximum in the same region as the unacetylated CTMP (λ , 370 nm, *Fig. 6a*). No shoulder at 415 nm was, however, observed, and the increase in absorption was less in the whole UV-visible region (cf. *Fig. 2a*). The two light sources that emitted light in both the ultraviolet and visible ranges induced photobleaching in the visible range. The absorption in the UV-part of the spectra was also less and shifted about 20 nm toward lower wavelengths (cf. *Figs. 2b-c* and *Figs. 6b-c*). The photobleaching resulted in a substantial brightness increase as can be seen in *Table 1*; the brightness values were 79-80% for the acetylated sheets compared to 60-62.5% for the controls after an intense aging for 312 and 349 hours. The reduced absorption at λ_{max} just below 400 nm (extending into the visible range) indicates that some of the colored structures formed on acetylation of high-brightness aspen CTMP most likely are readily photobleachable when subjected to a light source emitting light in the visible range. Also, the acetylated spruce CTMP, irradiated with the RPR 4190Å and RPR 5750Å UV/VIS-fluorescent lamps, removed structures contributing to the absorption just below 400 nm. The apparent absorption maximum at 425 nm observed for irradiated

unacetylated spruce CTMP was practically missing after acetylation, except for the low derivatized CTMP (see *Figs. 7b-c*).

These results indicate that acetylation slows down the UV-light induced reactions as seen for the RPR 3500Å UV-lamps aged CTMPs. However, acetylation promotes photobleaching reactions when subjected to an irradiation source emitting light in both the ultraviolet and visible regions, an effect that contributes to the improved stability toward light-induced aging. These results also indicate that different photochemical reactions occur, depending on the light source used for reversion, for acetylated pulps as well as for unacetylated pulps. It is therefore extremely important to use a light source that mimics the actual aging conditions as close as possible if an accurate picture of the yellowing phenomenon is going to be obtained. Further studies, using both unacetylated and acetylated model compounds incorporated on different types of high-yield pulps, are needed to fully explain the changes in the absorption difference spectra of acetylated and/or irradiated high-yield pulps.

Conclusions

This work demonstrated the usefulness of solid-state UV/VIS diffuse reflectance spectroscopy for the study of light-induced brightness reversion of untreated and chemically modified high-yield pulps. This work also showed the importance of the irradiation source used for accelerated aging because the photochemistry is strongly dependent of the wavelength distribution of the light source chosen.

Acetylation of aspen CTMP was found to generate a substantial increase in absorption in the entire wavelength region of 350-700 nm with maxima at approximately 370 and 430 nm, whereas the changes that took place during acetylation of the spruce CTMP were manifested as a decrease in absorption at wavelengths below 410 nm (maximum at 385 nm) and an increase in the absorption band centered at 455 nm.

UV-irradiation of aspen CTMP (unacetylated) introduced chromophores with an absorption maximum near 370 nm and with a shoulder at approximately 415 nm. When the aspen CTMP was irradiated with the UV/VIS lamps, a slight shift in the absorption peak to shorter wavelengths (λ_{max} ~360 nm) together with less absorption in the visible range was observed. The absorption difference spectra of UV-irradiated spruce CTMP displayed two absorption bands at 330 and 425 nm. In addition to these two bands, UV/VIS-irradiation induced photobleaching in the UV-part of the spectra extending into the visible range (λ_{max} ~390 nm). Acetylation of the pulps slowed down the UV-light induced chromophore formation, but could also promote photobleaching if the acetylated pulps were subjected to both UV-radiation and visible light.

It is difficult to assess the changes seen in the UV/VIS spectra to the formation/destruction of chromophoric and leucochromophoric structures in the lignin since i) most absorption data are given for simple model compounds in solution, and it is likely that the position of the absorption peaks may be different in the solid phase, and ii) the position of absorption maxima of the chromophoric and leucochromophoric structures may shift when incorporated in the lignin macromolecule. Further studies are therefore needed to determine the absorption characteristics of several classes of important structures when incorporated in different types of high-yield pulps.

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Figure captions

Fig. 1. Spectral characteristics of the tested irradiation sources. The spectral energy distributions of standard “cool white” fluorescent color (Waymouth 1992, dotted line) and natural daylight (Merrigan 1975, broken line) are given as a comparison.

Fig. 2. Absorption difference spectra of hydrogen-peroxide-bleached aspen CTMP after irradiation for various periods of time ($\Delta ABS = ABS_{\text{irradiated}} - ABS_{\text{unirradiated}}$). a: RPR 3500Å. b: RPR 4190Å. c: RPR 5750Å.

Fig. 3. Absorption difference spectra of hydrogen-peroxide-bleached spruce CTMP after irradiation for various periods of time ($\Delta ABS = ABS_{\text{irradiated}} - ABS_{\text{unirradiated}}$). a: RPR 3500Å. b: RPR 4190Å. c: RPR 5750Å.

Fig. 4. Absorption difference spectra of hydrogen-peroxide-bleached spruce CTMP ($\Delta ABS = ABS_{\text{irradiated}} - ABS_{\text{unirradiated}}$). RPR 3500Å: 7 h. RPR 4190Å: 349 h. RPR 5750Å: 312 h.

Fig. 5. Absorption difference spectra of hydrogen-peroxide-bleached aspen CTMP (solid line) and hydrogen-peroxide-bleached spruce CTMP (dotted line) after acetylation ($\Delta ABS = ABS_{\text{acetylated}} - ABS_{\text{unacetylated}}$). The numbers in brackets denote the acetylation time in minutes.

Fig. 6. Absorption difference spectra of hydrogen-peroxide-bleached aspen CTMP after acetylation (acetyl content: 8.1%) and subsequent irradiation for various periods of time ($\Delta ABS = ABS_{\text{acetylated, irradiated}} - ABS_{\text{acetylated, unirradiated}}$). The dotted line shows the absorption difference spectra for a low derivatized aspen CTMP (acetyl content: 3.9%). a: RPR 3500Å. b: RPR 4190Å. c: RPR 5750Å.

Fig. 7. Absorption difference spectra of hydrogen-peroxide-bleached spruce CTMP after acetylation (acetyl content: 9.6%) and subsequent irradiation for various periods of time ($\Delta ABS = ABS_{\text{acetylated, irradiated}} - ABS_{\text{acetylated, unirradiated}}$). The dotted line shows the absorption difference spectra for a low derivatized spruce CTMP (acetyl content: 4.4%). a: RPR 3500Å. b: RPR 4190Å. c: RPR 5750Å.

Table 1. Change in optical properties [TAPPI brightness ($R_{\infty 457}$), L^* -, a^* -, and b^* -values] on acetylation and light-induced aging of untreated and acetylated hydrogen-peroxide-bleached aspen CTMP and spruce CTMP. Acetylation times (min) are given within parentheses.

Pulp	Acetyl content, % by mass	Unirradiated			RPR 3500Å			RPR 4190Å			RPR 5750Å						
					Irradiation time: 2 h/7 h ^a			Irradiation time: 349 h			Irradiation time: 312 h						
		R _{∞457} %	L*	a*	b*	R _{∞457} %	L*	a*	b*	R _{∞457} %	L*	a*	b*				
<i>Aspen CTMP</i>																	
Control	0.6	84.3	96.4	-1.3	5.6	64.4	92.0	-1.8	14.4	62.6	90.6	0.0	13.6	60.0	89.8	-0.1	14.7
Acetylated (5) ^b	3.9	76.4	94.2	-1.0	8.0	63.4	91.7	-1.4	14.9	73.4	93.6	-0.4	9.4	72.7	93.6	-0.4	9.9
(20) ^b	8.1	73.1	93.6	-0.5	9.4	63.7	91.8	-0.8	14.8	80.2	95.1	-0.3	6.4	78.9	94.9	-0.4	7.1
<i>Spruce CTMP</i>																	
Control	0.5	77.8	95.5	-1.9	9.3	48.5	88.6	-1.8	24.4	48.5	87.1	-0.6	21.6	46.7	86.5	0.9	22.6
Acetylated (5) ^b	4.4	75.2	95.4	-1.8	11.1	51.8	90.4	-1.8	24.0	60.7	91.1	-0.7	16.4	60.4	90.8	-0.3	16.1
(20) ^b	9.6	73.3	95.0	-1.6	11.8	56.0	91.4	-2.0	21.4	73.1	93.8	-0.6	10.0	71.6	93.7	-0.7	11.0

^aThe data are given at an irradiation time of 2 hours and 7 hours for the aspen CTMP and spruce CTMP, respectively.

^bAcetylation temperature, 100°C.

Figure 1

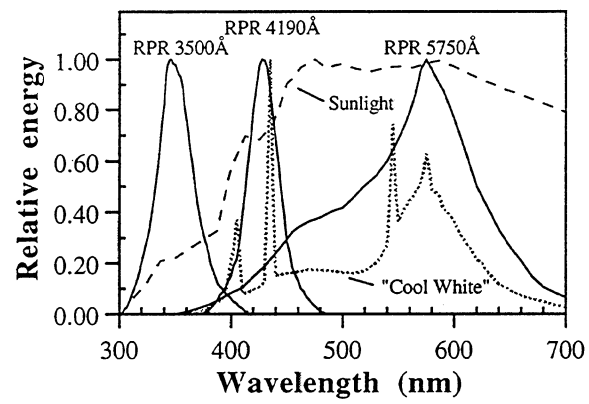


Figure 2a

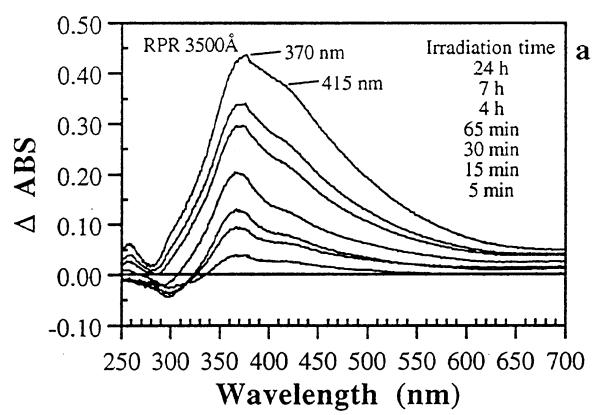


Figure 2b

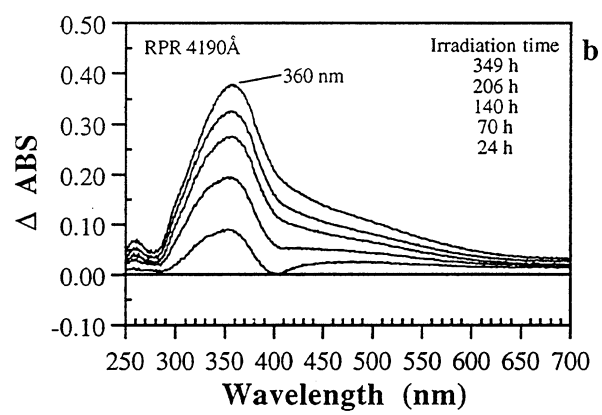


Figure 2c

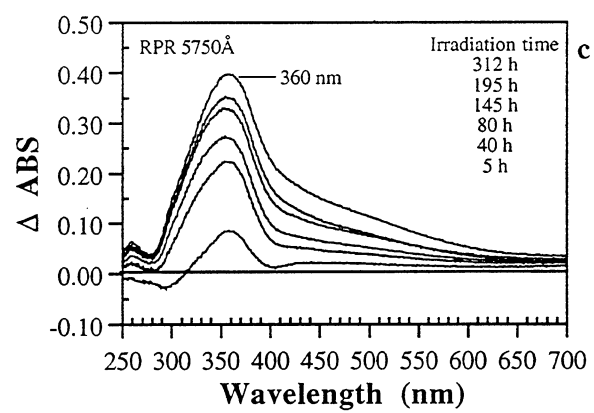


Figure 3a

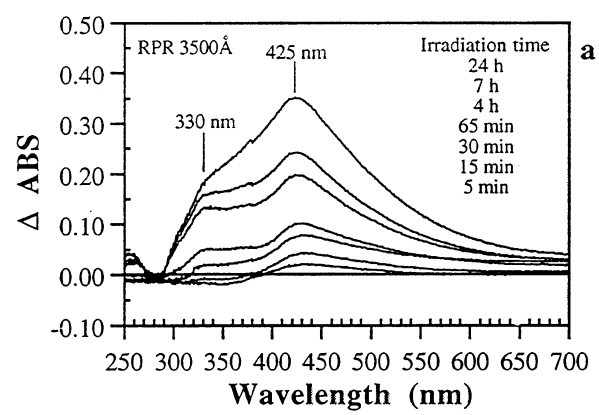


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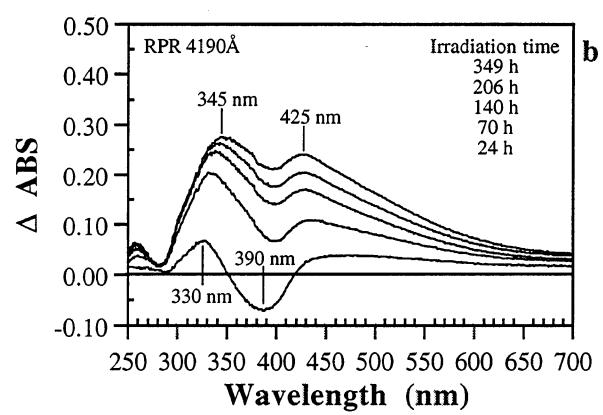


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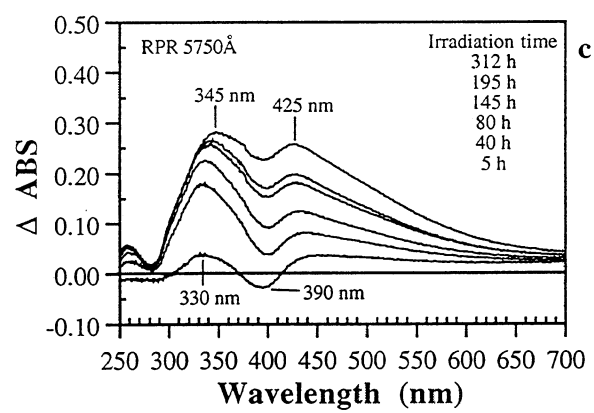


Figure 4

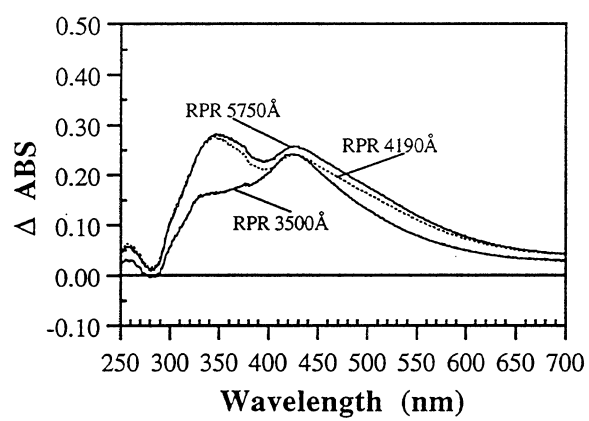


Figure 5

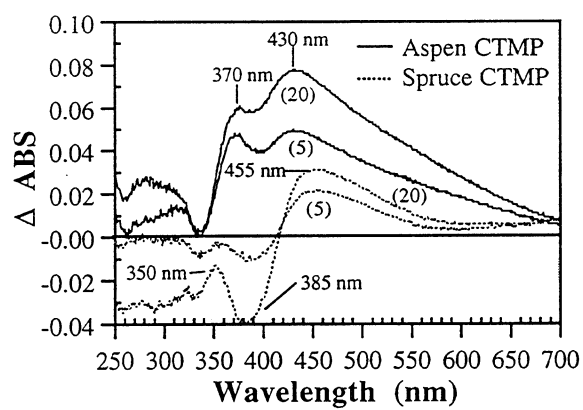


Figure 6a

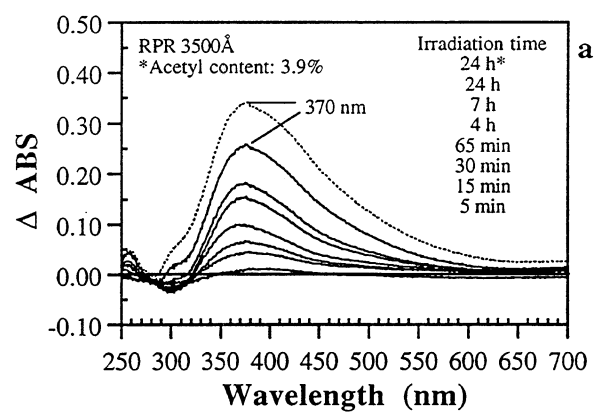


Figure 6b

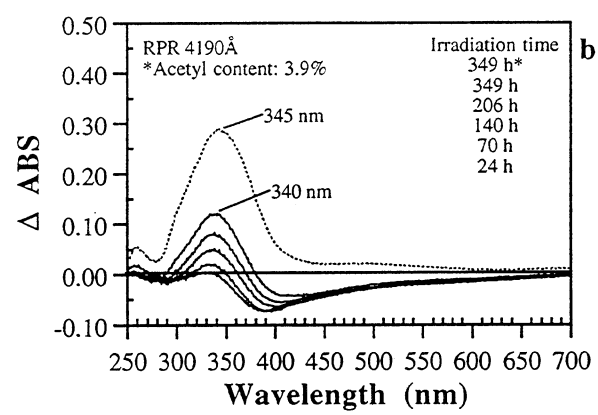


Figure 6c

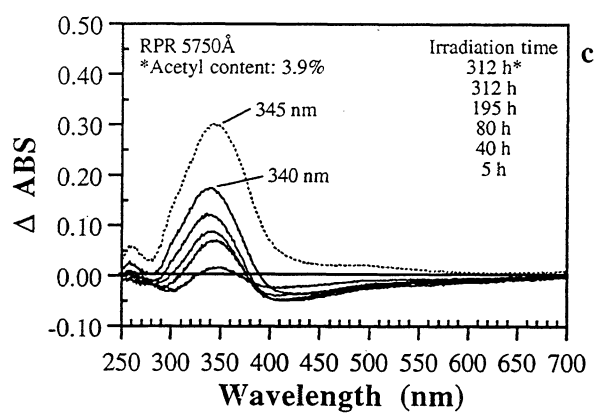


Figure 7a

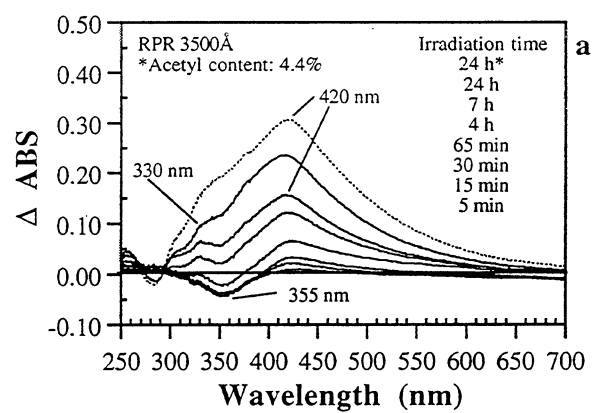


Figure 7b

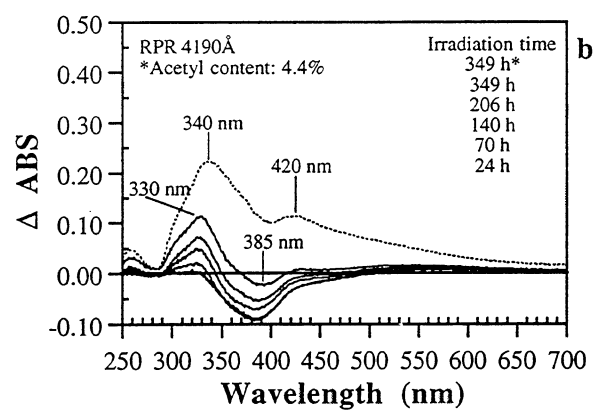


Figure 7c

